VERIFICATION OF TRANSLATION

The undersigned translator, having an address at Bridgestone Toranomon Building 6F, 25-2, Toranomon 3-chome, Minato-ku, Tokyo, 105-0001 Japan declares that:

(1) I am fully conversant both with the Japanese and English language.

(2) I have translated into English the Japanese Patent Application No. 2000-127336 filed on April 27, 2000. A copy of said English translation is attached hereto.

(3) The translation is to the best of my knowledge and belief, an accurate translation of the application as filed into the English language.

The undersigned declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief believed to be true.

Date: September 9, 2003

Tamotsu Ohtani

Tamotsu Ohtani

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy of the following application as filed with this office.

Date of Application: April 27, 2000

Application Number: Patent Application No. 2000-127336

Applicant: Idemitsu Petrochemical Co., Ltd.

May 31, 2001

Commissioner,
Patent Office

Kozo Oikawa

Certification Number 2001-3048593

[Document] Patent Application

[Reference No.] N00-0023

[Addressee] Commissioner of the Patent Office

[International Patent Classification] C08L 69/00

G11B 7/24

[Title of the invention]

Polycarbonate resin for optical disk substrates and the optical disk substrate

[Inventor]

[Address] 1-1, Anesakikaigan, Ichihara-shi, Chiba-ken

[Name] Tatsuya TOMIOKA

[Inventor]

[Address] 1-1, Anesakikaigan, Ichihara-shi, Chiba-ken

[Name] Hiroshi KAWATO

[Inventor]

[Address] 6-1, Shiba 5-chome, Minato-ku, Tokyo

[Name] Munehiro CHOSA

[Applicant]

[Identification No.] 000183657

[Name] Idemitsu Petrochemical Co., Ltd.

[Attorney]

[Identification No.] 100081765

[Patent Attorney]

[Name] Masamichi TOHEI

[Indication of Fee]

[Payment Register No.] 041472

[Amount of Payment] ¥21,000

[List of Item Filed]

[Item] Specification 1

[Item] Abstract 1

[General Power of Attorney No.] 0000758

[Requirement of Proof] Yes

[Document] Specification

[Title of Invention] Polycarbonate resin for optical disk substrates and the optical disk substrate

[Claims]

[Claim 1] A polycarbonate resin for an optical disk substrate characterized by having a viscosity average molecular weight of from 10,000 to 17,000, an iron content of 0.2 ppm or less and a free total phenol content of 80 ppm or less, and containing from 100 to 500 ppm of a releasing agent.

[Claim 2] A polycarbonate resin for an optical disk substrate described in claim 1, which has an acetone soluble content of 12% by mass or less.

[Claim 3] A polycarbonate resin for an optical disk substrate described in claim 1 or 2, which contains from 150 to 350 ppm of a releasing agent.

[Claim 4] A polycarbonate resin for an optical disk substrate described in any of claims 1 to 3, wherein the releasing agent is a polyhydric alcohol fatty acid ester.

[Claim 5] An optical disk substrate comprising a polycarbonate resin for an optical disk substrate described in any of claims 1 to 4.

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs]

The present invention relates to a polycarbonate resin for an optical disk substrate and an optical disk substrate, and more

particularly, it relates to a polycarbonate resin that is suitable for a material of an optical disk substrate having less defects due to flash, and an optical disk substrate formed with the resin.

[0002]

[Description of the Prior Art] A polycarbonate resin is widely used as a substrate of an optical disk, such as CD, CD-ROM, MO, CD-R, CD-RW, DVD-ROM, DVD-R and DVD-RAM, owing to the transparency, the heat resistance and the low water absorbing property thereof. In general, these optical disks are often produced by such a process that a surface formed by engraving signals, such as pits and grooves, on a thin plate of nickel called as a stamper arranged in a metallic mold is transferred to a substrate formed with a polycarbonate resin through injection molding.

[0003] In the production of a substrate of an optical disk in recent years, several tens to a number exceeding one hundred of molding machines are introduced in one factory to further enhance the mass production volume efficiency, and simultaneously quality control is severely ensured. However, although there is no change of a stamper or no change in molding conditions, and the factors determining the flowability of a polycarbonate resin, such as the molecular weight, the molecular weight distribution, the glass transition temperature and the like, are stable within prescribed ranges, there are some cases where releasing failure extemporaneously occurs upon sprue cutting of

a center hole of a disk substrate, and the outer circumference of the disk substrate or fine flash formed on the outer circumference is in friction with a metallic mold due to the releasing failure to cause contamination of resin dusts, whereby the yield of the disk substrates is decreased to several percents to several tens percents. The phenomenon is generally referred to as a defect due to flash, which can be prevented by increasing an amount of a releasing agent. However, the amount of the releasing agent cannot be increased to an unnecessary level because there is a tendency of occurrence of defects on optical characteristics, particularly such a tendency that occurrence of defects of polarization and white turbidity in the polycarbonate resin is accelerated upon an accelerated aging test under constant temperature and humidity, whereby the reliability of storage stability of recorded data as an optical disk is also lowered.

[0004]

[Problem(s) to be Solved by the Invention]

The invention has been developed under the circumstances, and is to provide a polycarbonate resin that is suitable for a material of an optical disk substrate having less defects due to flash without increase of an addition amount of a releasing agent to an unnecessary level, and an optical disk substrate formed with the resin.

[0005]

[Means for Solving the Problem]

As a result of various investigations made by the inventors, it has been found that occurrence of defects due to flash is correlated with an amount of iron and a free total phenol content in a polycarbonate resin, and thus the first invention to the fourth invention have been completed.

[0006]

That is, the summary of this invention is as follows.

1. A polycarbonate resin for an optical disk substrate characterized by having a viscosity average molecular weight of from 10,000 to 17,000, an iron content of 0.2 ppm or less and a free total phenol content of 80 ppm or less, and containing from 100 to 500 ppm of a releasing agent.
2. A polycarbonate resin for an optical disk substrate described in above 1, which has an acetone soluble content of 12% by mass or less.
3. A polycarbonate resin for an optical disk substrate described in above 1 or 2, which contains from 150 to 350 ppm of a releasing agent.
4. A polycarbonate resin for an optical disk substrate described in any of above 1 to 3, wherein the releasing agent is a polyhydric alcohol fatty acid ester.
5. An optical disk substrate comprising a polycarbonate resin for an optical disk substrate described in any of above 1 to 4.

[0007]

[Embodiments of the Invention]

A polycarbonate resin used in an optical disk substrate of

the first invention (sometimes simply referred to as an "invention" in this chapter) will be described.

The chemical structure and the production process of the polycarbonate resin are not particularly limited, and various kinds thereof can be used. For example, an aromatic polycarbonate resin produced through a reaction between a dihydric phenol and a carbonate precursor is preferably used. The production process that can be used may be either the solution process or the molten process.

[0008] The dihydric phenol includes various kinds thereof, and preferred examples thereof include 2,2-bis(4-hydroxyphenyl)propane, bis(4-hydroxyphenyl)methane, 1,1-bis(4-hydroxyphenyl)ethane, 2,2-bis(4-hydroxy-3,5-dimethylphenyl)propane, 4,4'-dihydroxydiphenyl, bis(4-hydroxyphenyl)cyclohexane, bis(4-hydroxyphenyl)ether, bis(4-hydroxyphenyl)sulfide, bis(4-hydroxyphenyl)sulfone, bis(4-hydroxyphenyl)sulfoxide, bis(4-hydroxyphenyl)ketone, hydroquinone, resorcin, catechol and the like. Among these dihydric phenols, a bis(hydroxyphenyl)alkane, particularly 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), is preferred. These dihydric phenols may be used solely or in combination of two or more of them through mixing.

[0009] As the carbonate precursor, a carbonyl halide, a carbonyl ester and a haloformate can be used. More specific examples thereof include phosgene, dihaloformate of a dihydric phenol, diphenyl carbonate, dimethyl carbonate, diethyl carbonate and

the like.

[0010] With respect to the chemical structure of the polycarbonate resin, those having a molecular chain having a linear structure, a cyclic structure or a branched structure can be used. Among these, as the polycarbonate resin having a branched structure, those produced by using, as a branching agent, 1,1,1-tris(4-hydroxyphenyl)ethane,
α,α',α"-tris(4-hydroxyphenyl)-1,3,5-triisopropylbenzene, fluoroglycine, trimellitic acid, isatin bis(o-crezol) and the like are preferably used. A polyester polycarbonate resin produced by using a bifunctional carboxylic acid, such as terephthalic acid and the like, or an ester forming derivative thereof can be used as the polycarbonate resin. Furthermore, a mixture of these polycarbonate resins having various chemical structures can be used.

[0011] The viscosity average molecular weight of the polycarbonate resin is generally from 10,000 to 30,000. The viscosity average molecular weight (Mv) is a value obtained in such a manner that a viscosity of an methylene chloride solution at 20°C is measured by using an Ubbelohde viscometer to obtain a limiting viscosity [η], and the value is calculated by the equation $[\eta] = 1.23 \times 10^{-5}\ Mv^{0.83}$. For the adjustment of the molecular weight of the polycarbonate resin, phenol, p-tert-butylphenol, p-tert-octylphenol, p-cumylphenol and the like are used.

[0012] As for the polycarbonate resin, the solution process is

generally employed, and thus it will be described under assumption where it is obtained by the solution process.

It is necessary that flakes of a polycarbonate resin produced by the foregoing process are subjected to an elution treatment by using a solvent, such as acetone, dioxane and the like, so as to elute impurities and free total phenol. In this case, it is sufficient that the elution treatment is carried out in the state of pellets, so as to provide a viscosity average molecular weight of from 10,000 to 17,000, an iron content of 0.2 ppm or less and a free total phenol content of 80 ppm or less. It is preferred that the acetone soluble content is 12% by mass or less. A releasing agent and, depending on necessity, from 20 to 100 ppm of a phosphorous antioxidant are added to the dried polycarbonate resin flakes after the elution treatment, and it is then pelletized by an extruder. It is necessary that the releasing agent in the pellets is from 100 to 500 ppm (preferably from 150 to 350 ppm).

When the releasing agent is less than 100 ppm, occurrence of defects due to flash caused by releasing failure is increased, whereas when it exceeds 500 ppm, defects of polarization and white turbidity as an optical disk are liable to be occur, and thus both cases are not preferred.

[0013] As the releasing agent, a polyhydric alcohol fatty acid ester is preferably used, and examples thereof include a partial ester of a trihydric alcohol, such as glycerin, trimethylpropane, hexanetriol and the like, and a tetrahydric or more valence of

alcohol, such as pentaerythritol, mesoerythritol, xylitol, sorbitol and the like, with a fatty acid having a carbon number of from 10 to 30. Examples of the fatty acid include capric acid, undecanoic acid, lauric acid, tridecanoic acid, myristic acid, pentadecanoic acid, palmitic acid, margaric acid, stearic acid, nonadecanoic acid, eicosanoic acid, behenic acid and the like. Specifically, a glycerin monoester, such as glycerin monostearate, glycerin monopalmitate, glycerin monomyristate, glycerin mono laurate and the like, pentaerythritol distearate, pentaerythritol tristearate, pentaerythritol monopalmitate, pentaerythritol dipalmitate, mesoerythritol trilaurate, xylitol trilaurate, xylitol distearate, xylitol tristearate, xylitol tetrastearate and the like are used. These esters may be used singly or in combination of two or more of them.

[0014] Examples of the phosphorous antioxidant include a trialkyl phosphite, such as trimethyl phosphite, triethyl phosphite, tributyl phosphite, trioctyl phosphite, trinonyl phosphite, tridecyl phosphite, trioctadecyl phosphite, distearylpentaerythtyl diphosphite, tris(2-chloroethyl)phosphite, tris(2,3-dichloropropyl)phosphite and the like; a tricycloalkyl phosphite, such as tricyclohexyl phosphite and the like; a triaryl phosphite, such as triphenyl phosphite, tricresyl phosphite, tris(ethylphenyl) phosphite, tris(butylphenyl) phosphite, tris(nonylphenyl) phosphite, tris(hydroxyphenyl) phosphite and the like; a monoalkyldiaryl phosphite, such as

2-ethylhexyldiphenyl phosphite; a trialkyl phosphate, such as trimethyl phosphate, triethyl phosphate, tributyl phosphate, trioctyl phosphate, tridecyl phosphate, trioctadecyl phosphate, distearylpentherythtyl diphosphate, tris(2-chloroethyl) phosphate, tris(2,3-dichloropropyl) phosphate and the like; a tricycloalkyl phosphate, such as tricyclohexyl phosphate and the like; a triaryl phosphate, such as triphenyl phosphate, tricresyl phosphate, tris(nonylphenyl) phosphate, 2-ethylphenyl diphenyl phosphate and the like; and the like. These may be used solely or in combination of two or more kinds of them.

[0015] As described in the foregoing, it is necessary that the polycarbonate resin has, in the state of pellets, a viscosity average molecular weight of from 10,000 to 17,000, an iron content of 0.2 ppm or less, and a free total phenol content of 80 ppm or less. When the residual iron content and the free total phenol content are too large, defects due to flash frequently occur. It is preferred that the acetone soluble content is 12% by mass or less from the standpoint of prevention of occurrence of defects due to flash.

When the viscosity average molecular weight is less than 10,000, the mechanical strength of the molded article is lowered, whereas when it exceeds 17,000, distortion remains in the molded article due to shortage of flowability upon molding, so as to lower the optical characteristics, and therefore both the cases are not preferred. The measurement methods of the iron content, the free total phenol content and the acetone soluble content

are as follows.

[0016]

(1) Iron Content

After ashing a sample, it is quantitatively analyzed by the graphite furnace atomic absorption spectrometry.

(2) Free Total Phenol Content

It is the total amount of the phenols, such as the dihydric phenol of the raw material monomer, the monohydric phenol of the terminating agent and the like, and is analyzed by the following method.

(1) 10 g of a sample is put in cylindrical filter paper.

(2) 120 cc of acetone and 2 or 3 pieces of glass zeolite are put in a flat-bottom flask.

(3) Soxhlet extraction is carried out. The extraction time in the case of pellets is 4 hours from the point where the first acetone reflux is completed.

(4) The acetone solution is set in a rotary evaporator, and acetone is distilled off and concentrated to dry.

(5) After drying at 105°C for one hour in a dryer, it is stood to cool to room temperature.

(6) The content is dissolved by adding 10 cc of methylene chloride.

(7) 50 cc of a 0.1 N sodium hydroxide aqueous solution is added and stirred with a stirrer for 15 minutes.

(8) The content is stood to be separated, and about 25 cc of the sodium hydroxide solution as the aqueous layer (upper

layer) is collected and filtered with 5A filter paper.

(9) The total phenol content of the filtrate is measured by a spectrophotometer.

[0017]

(3) Acetone Soluble Content

(1) 1 g of a sample is dissolved in 10 cc of methylene chloride.

(2) 200 cc of acetone is added thereto to precipitate polycarbonate.

(3) The polycarbonate is removed by filtration.

(4) After concentrating the filtrate to dry, the weight is measured and is then designated as the acetone soluble content.

The optical disk substrate of the invention can be obtained by molding the polycarbonate pellets in an arbitrary method, such as the injection molding method, a compacting molding method, the extrusion molding method and the like. Among these, the injection molding method using a stamper is preferred.

The invention will be then described more specifically with reference to examples and comparative examples.

[0018]

[Example]

(Example 1)

To 100 kg of polycarbonate in a flake form having an acetone soluble content of 14% by mass and a free total phenol content of 120 ppm produced by the solution process by using bisphenol A and phosgene as raw materials, 225 kg of acetone was added and

stirred at 50°C for one hour to carry out an elution treatment. Thereafter, acetone was removed, and it was dried at 120°C under reduced pressure of from 1.3 to 40 hPa for 20 hours. The resulting polycarbonate a flake form had a viscosity average molecular weight of 14,900, to which 300 ppm of glycerin monostearate as a releasing agent and 40 ppm of tris(2,4-di-t-butylphenyl)phosphite as a phosphorous antioxidant were added, and then extruded to be pelletized. The pellets had an acetone soluble content of 8% by mass, a free total phenol content of 70 ppm and an iron content of 0.1 ppm, and contained 280 ppm of glycerin monostearate. The pellets were fed to an injection molding machine (DISK5, produced by Sumitomo Heavy Industries, Ltd.), and 600 pieces of disk substrates having a diameter of 130 mm and a thickness of 1.2 mm under the following conditions.

Cylinder temperature: 325°C

Metallic mold temperature: 90°C (stamper side)/85°C

Stamper: for CD-ROM

The resulting disk substrates were examined with a flaw defect inspection machine, and as a result, the defects due to flash were 4.5%. The disk substrates were subjected to accelerated deterioration under constant temperature and humidity of 90°C and 90% for 300 hours, and the block error rate was 5 when they were measured with an electric characteristics inspection machine.

[0019]

(Example 2)

To 100 kg of polycarbonate in a flake form having an acetone soluble content of 12% by mass and a free total phenol content of 120 ppm produced by the solution process by using bisphenol A and phosgene as raw materials, 225 kg of acetone was added and stirred at 60°C for one hour to carry out an elution treatment. Thereafter, acetone was removed, and it was dried at 120°C under reduced pressure of from 1.3 to 40 hPa for 20 hours. The resulting polycarbonate a flake form had a viscosity average molecular weight of 14,900, to which 300 ppm of glycerin monostearate as a releasing agent and 40 ppm of tris(2,4-di-t-butylphenyl)phosphite as a phosphorous antioxidant were added, and then pelletized with an extruder. The pellets had an acetone soluble content of 6% by mass, a free total phenol content of 40 ppm and an iron content of 0.1 ppm, and contained 280 ppm of glycerin monostearate. The pellets were formed into 600 pieces of disk substrates in the same manner as in Example 1. The resulting disk substrates were examined with a flaw defect inspection machine, and as a result, the defects due to flash were 2.5%.

[0020]

(Comparative Example 1)

To polycarbonate in a flake form having an acetone soluble content of 14% by mass, a free total phenol content of 120 ppm and a viscosity average molecular weight of 14,900 produced by the solution process by using bisphenol A and phosgene as raw

materials, 300 ppm of glycerin monostearate as a releasing agent and 40 ppm of tris(2,4-di-t-butylphenyl)phosphite as a phosphorous antioxidant were added, and then pelletized with an extruder. The pellets had an acetone soluble content of 13% by mass, a free total phenol content of 90 ppm and an iron content of 0.1 ppm, and contained 280 ppm of glycerin monostearate. The pellets were formed into 600 pieces of disk substrates in the same manner as in Example 1. The resulting disk substrates were examined with a flaw defect inspection machine, and as a result, the defects due to flash were 15%.

[0021]

(Comparative Example 2)

To 100 kg of polycarbonate in a flake form having an acetone soluble content of 14% by mass and a free total phenol content of 120 ppm produced by the solution process by using bisphenol A and phosgene as raw materials, 225 kg of acetone was added and stirred at 50°C for one hour to carry out an elution treatment. Thereafter, acetone was removed, and it was dried at 120°C under reduced pressure of from 1.3 to 40 hPa for 20 hours. The resulting polycarbonate a flake form had a viscosity average molecular weight of 14,900, to which 50 ppm of glycerin monostearate as a releasing agent and 40 ppm of tris(2,4-di-t-butylphenyl)phosphite as a phosphorous antioxidant were added, and then pelletized with an extruder. The pellets had an acetone soluble content of 8% by mass, a free total phenol content of 80 ppm and an iron content of 0.1 ppm,

and contained 40 ppm of glycerin monostearate. The pellets were formed into 600 pieces of disk substrates in the same manner as in Example 1. The resulting disk substrates were examined with a flaw defect inspection machine, and as a result, the defects due to flash were 11.0%.

[0022]

(Comparative Example 3)

To 100 kg of polycarbonate in a flake form having an acetone soluble content of 14% by mass and a free total phenol content of 120 ppm produced by the solution process by using bisphenol A and phosgene as raw materials, 225 kg of acetone was added and stirred at 50°C for one hour to carry out an elution treatment. Thereafter, acetone was removed, and it was dried at 120°C under reduced pressure of from 1.3 to 40 hPa for 20 hours. The resulting polycarbonate a flake form had a viscosity average molecular weight of 14,900, to which 600 ppm of glycerin monostearate as a releasing agent and 40 ppm of tris(2,4-di-t-butylphenyl)phosphite as a phosphorous antioxidant were added, and then pelletized with an extruder. The pellets had an acetone soluble content of 8% by mass, a free total phenol content of 80 ppm and an iron content of 0.1 ppm, and contained 550 ppm of glycerin monostearate. The pellets were formed into 600 pieces of disk substrates in the same manner as in Example 1. The resulting disk substrates were examined with a flaw defect inspection machine, and as a result, the defects due to flash were 4.0%, but after the disk substrates were

subjected to accelerated deterioration under constant temperature and humidity of 90°C and 90% for 300 hours, the block error rate was 25 when they were measured with an electric characteristics inspection machine.

[0023]

[Effect of the Invention] According to this invention, the optical disk substrate by which the defect in a flash comes to fabricate the polycarbonate resin constituent and this resin constituent which were suitable as a material of a few optical disk substrate can be offered, without increasing the addition of a release agent more than required.

[Document] Abstract

[Abstract]

[Objects]

This invention aims at offering the optical disk substrate which the defect in a flash becomes from the polycarbonate resin and this resin which were suitable as a material of a few optical disk substrate, without having been made in view of the above-mentioned situation, and increasing the addition of a release agent more than required.

[Means for Solving the Problems]

Polycarbonate resin for optical disk substrates which viscosity average molecular weights are 10,000-17,000, and 0.2 ppm or less and the amount of isolation total phenols is [the amount of iron] 80 ppm or less, and is characterized by containing 100-500 ppm of release agents. The optical disk substrate which consists of polycarbonate resin for optical disk substrates according to polycarbonate resin for optical disk substrates

[Selected Drawings] None